

AD-A085 523

ILLINOIS UNIV AT CHICAGO CIRCLE DEPT OF CHEMISTRY
HIGH ENERGY MATERIALS. NEW PREPARATION APPROACHES TO NITRO AND --ETC(U)
JUN 80 J H BOYER N00014-79-C-0353

F/G 7/3

UNCLASSIFIED

NL

[W] +
AD-A085 523



END
DATE
FILMED
8-80
DTIC

ADA 085523

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

13

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER (6)	2. GOVT ACCESSION NO. AD-A085523	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) High Energy Materials, New Preparation Approaches to Nitro and Nitroso Derivatives.		5. TYPE OF REPORT & PERIOD COVERED Annual April 1, 1979 March 31, 1980
7. AUTHOR(s) (10) J. H. Boyer		8. CONTRACT OR GRANT NUMBER(s) NO0014-79-C-0353
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Illinois Chicago, Illinois		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Dr. Richard Miller, ONR Arlington, Virginia		12. REPORT DATE (11) 1 June 1980
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 16		13. NUMBER OF PAGES
LEVEL II		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) As Directed By ONR.		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) (9) Annual rept.		
18. SUPPLEMENTARY NOTES 1 Apr 79-31 Mar 80		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) High energy materials; nitro, nitroso, and cyano compounds.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Progress on the preparation of dinitro-dicyanoethylene from diaminomaleo-nitrile, from dicyanofuroxan, from dicyanoglyoxime and from nitroacetonitrile is discussed.		

This document has been approved for public release and sale; its distribution is unlimited.

DTIC ELECTED
JUN 16 1980
S C

175730

Jim

DDC FILE COPY

80 6 13 001

ANNUAL REPORT

HIGH ENERGY MATERIALS. NEW PREPARATION APPROACHES TO NITRO AND NITROSO
DERIVATIVES.

INSTITUTION: University of Illinois, Chicago

CONTRACT: N00014-79-C-0353

PRINCIPAL INVESTIGATOR:

Prof. J. H. Boyer
Department of Chemistry
University of Illinois
Chicago Circle Campus
Chicago, Illinois 60680
Tel (312) 996-2350
996-3161

PERIOD COVERED: 4/1/79 - 3/31/80

PERSONNEL: Dr. V. T. Ramakrishnan
(Senior Post-Doctoral (Assoc.))

Dr. T. P. Pillai
(Post-Doctoral Assoc.)

Approved for public release; distribution unlimited.

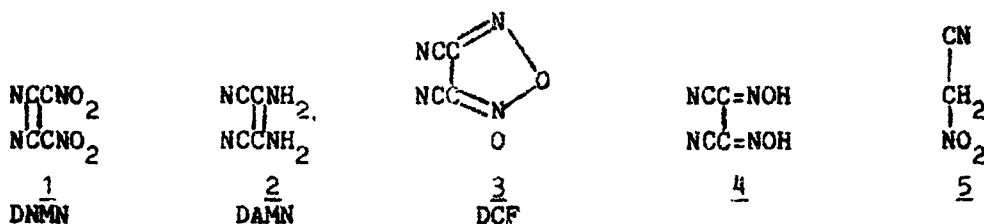
Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

Research sponsored by the Office of Naval Research.

Summary

Four routes were chosen to investigate the preparation of dinitrodicyanoethylene 1.

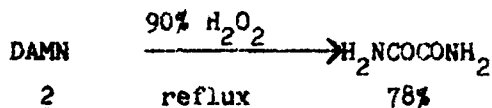
1. Oxidation of diaminomaleonitrile 2.
2. Oxidation of dicyanofuroxan 3.
3. Oxidation of the dioxime 4 of dioxosuccinonitrile.
4. Dehydrodimerization of nitroacetonitrile 5.



Progress along the first and last of these four routes indicates that the goal will soon be achieved.

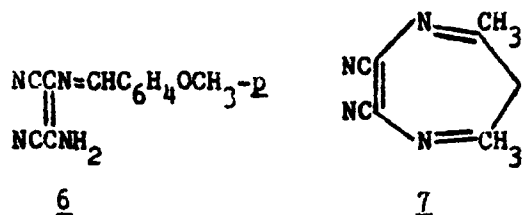
1. Oxidation of DAMN, 2.

Commercially available diaminomaleonitrile when treated with trifluoroperacetic acid did not give an isolable product. When refluxed in 90 percent hydrogen peroxide in acetone solution for 2 hrs, oxamide was isolated in 78 percent yield.

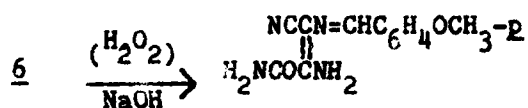


Literature methods ¹⁻⁴ were followed to prepare the monoimine 6 and the cyclic bisimine 7.

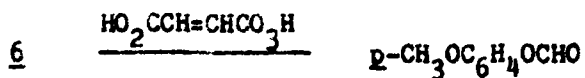
Accession Per	<input type="checkbox"/>			
By	Dist	Availability Codes	Award and/or special	
Justification				



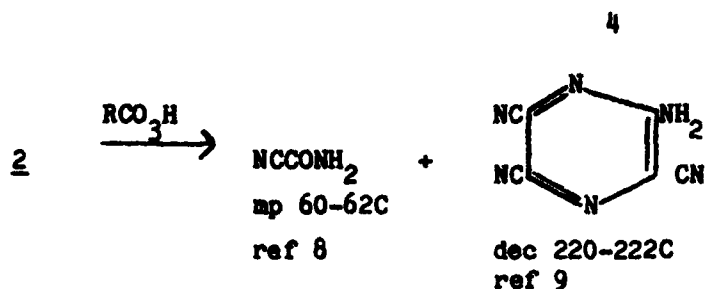
The imine 6 was unreactive toward neutral hydrogen peroxide (90 percent) in refluxing tetrahydrofuran. Both acidic hydrogen peroxide and *m*-chloroperbenzoic acid, MCPBA, consumed the imine 6 but analyses of the complex mixtures were unrewarding. According to a general method for the hydration of a nitrile, ^{5,6} alkaline hydrogen peroxide transformed the imine 6 into a known amide.⁶



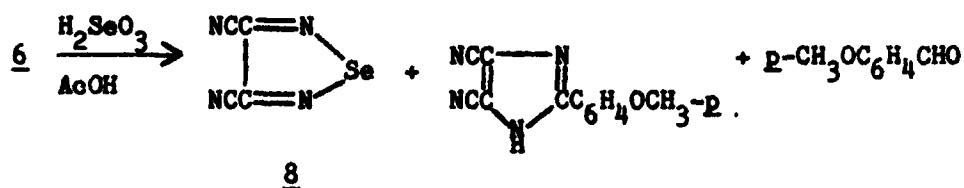
Although permaleic acid has been recommended for the oxidation of a primary amino group into a nitro group,⁷ it hydrolyzed, oxidized and rearranged the imine 6 into *p*-methoxyphenyl formate without a trace of the formation of a nitro compound.



Permaleic acid transformed DAMN, 2, into cyanoformamide and 2,5,6-tricyano-3-aminopyrazine.

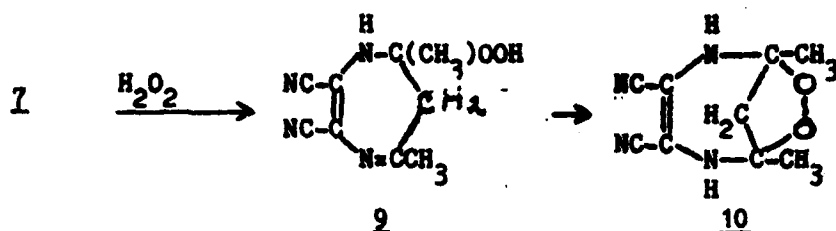


Selenous acid in hot acetic acid smoothly oxidized the imine 6 into 3,4-dicyanoselenadiazole, 8,¹⁰ 2- (p-methoxyphenyl)-4,5-dicyanoimidazole and anisaldehyde.

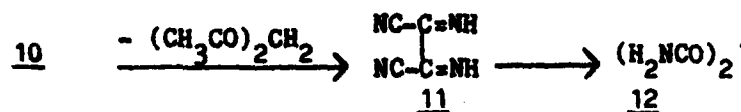


Singlet oxygen, a chromium (IV) complex, ceric ammonium nitrate and trifluoroperoxyacetic acid were each unreactive to the selenadiazole 8.

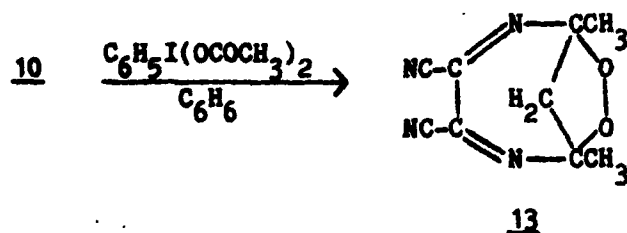
Peroxidation of the bisimine 7 gave considerably better results, although a simple treatment with MCPBA gave an intractable mixture. Neutral hydrogen peroxide in a mixture of methanol and acetonitrile gave oxamide in 40 percent yield whereas the cyclic peroxide 10, 80 percent yield, dec 125-126°C, with only traces of oxamide, was produced by the same reaction in acetonitrile (methanol not present). The peroxide 10 was also the major product, 74 percent yield, when the bisimine 7 was treated with hydrogen peroxide in methanol which contained a tertiary amine or a trace of alkali. Apparently an intermediate hydroperoxide 9 was involved.



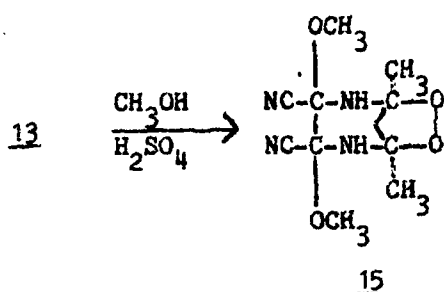
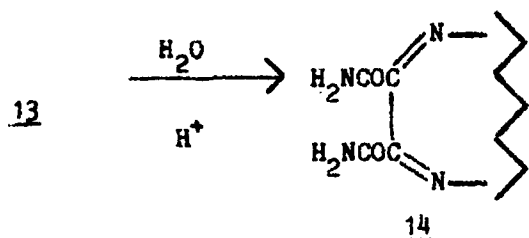
A slow spontaneous thermolysis of the peroxide 10 became rapid on heating and gave 2,4-pentanedione presumably with diiminosuccinonitrile 11. Hydrogen peroxide also reacted with the cyclic peroxide 10 to produce the diketone as well as oxamide 12.



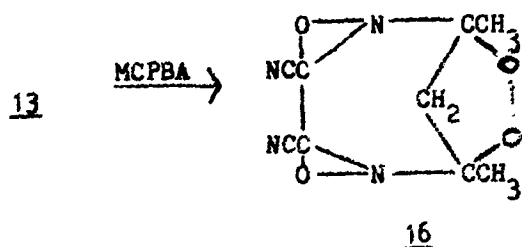
Iodobenzene diacetate in benzene quantitatively dehydrogenated the peroxide 10 into a new cyclic peroxide 13. The latter also produced 2,4-pentanedione on thermolysis (presumably undetected cyanogen was also formed).



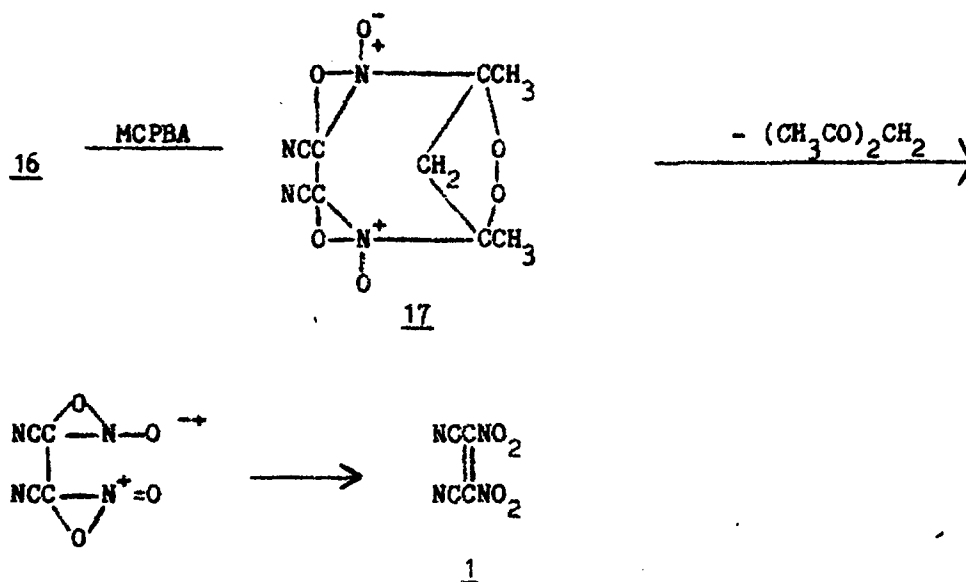
Hydration of compound 13 during chromatography (silica gel) gave the diamide 14. A related reaction with methanol gave the adduct 15.



MCPBA in acetone transformed the bisimine 13 into a bisoxaziridine 16 in moderate yield.



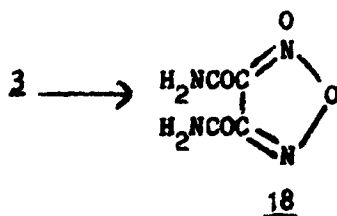
Peroxidation of the bisoxaziridine 16 is under investigation. An oxidative fragmentation of intermediate 17 into DNMN, 1, is anticipated as shown.



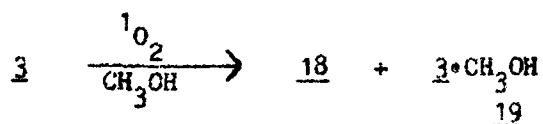
Molecular formulas for new compounds 10, 13, 14, 15, and 16 have been confirmed by elemental analyses for C, H, N and sometimes O; by mass spectrometry (for m w and/or fragment ions); and by nmr and ir spectroscopy. An isolated oxidation product from compound 16 and MCPBA has not been fully characterized. According to nmr and ir analysis it contains no hydrogen.

2. Oxidation of DCF, 3

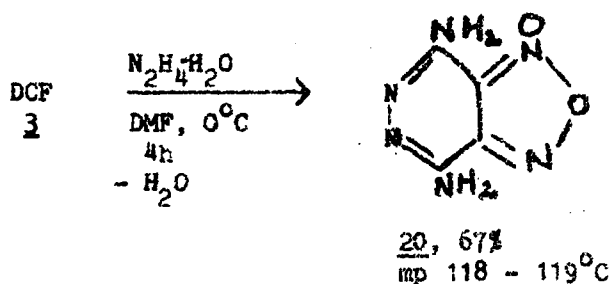
DCF, ¹¹3, absorbed on an alumina column gave the diamide 18 almost quantitatively on elution with methanol. Slightly lower yields were obtained when 3 was treated with oleum with or without hydrogen peroxide.



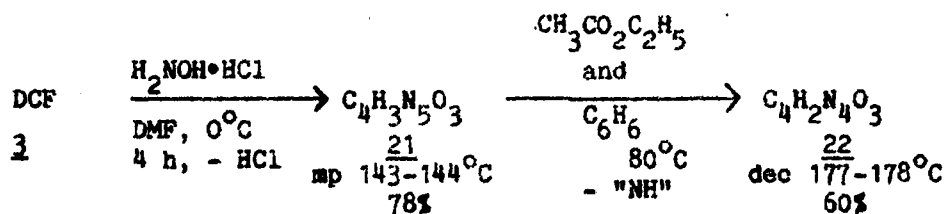
Singlet oxygen in methanol gave a mixture after workup, of the diamide 18 and an unspecified methanol adduct 19.



DCF and hydrazine (85%) in dimethyl formamide gave a pyridazino-furoxan 20.



An adduct 21 between DCF and hydroxylamine was obtained by treatment with hydroxylamine hydrochloride in DMF. When warmed in a mixture of ethyl acetate and hexane the adduct apparently lost a nitrogen and a hydrogen atom to give a new compound 22.



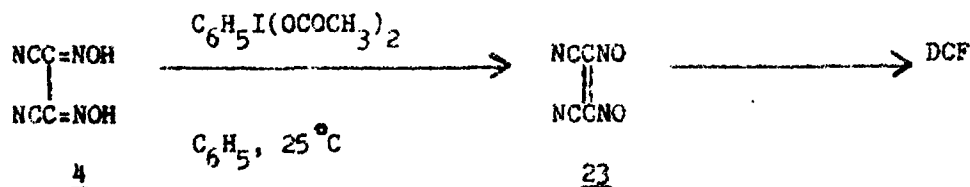
The diamide 18 resisted reaction with both hydrazine and hydroxylamine under similar circumstances.

Further characterization, including oxidation, of compounds 21 and 22 is underway.

DCF,3, has resisted attempts to open the furoxan ring by oxidation, although considerable progress has been realized in the peroxidation of benzofuroxans into corresponding o-dinitrobenzenes in a project not supported by ONR.

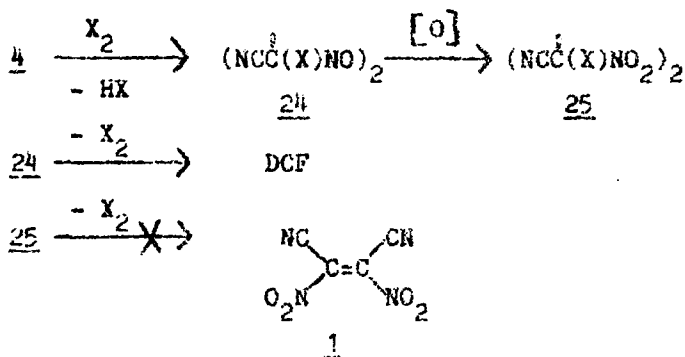
3. Oxidation of the Dioxime 4.

The dioxime 4 of dioxosuccinonitrile was prepared according to a literature procedure.¹² When treated with iodobenzene diacetate (recommended for dehydrogenation)¹³ in benzene solution at room temperature it was slowly converted into DCF. A similar reaction between the dioxime 4 and iodobenzene diacetate rapidly occurred even in a mixture of the solids to give DCF. The formation of DCF probably proceeded from the transient dinitroso compound 23.



The dioxime 4, when heated with iodobenzene diacetate in the presence of 90 percent hydrogen peroxide in acetone, gave a solid product melting at 134-135°C. A high oxygen content was indicated by the empirical formula CH_2O . The structure of this compound is under investigation.

Halogenation of the dioxime 4 followed by oxidation and dehalogenation was a conceivable sequence for the proposed formation of dicyanodinitroethylene, 1.

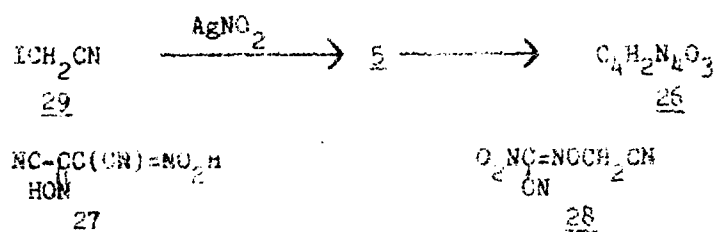


When the dioxime 4 was treated with a suspension of sodium bicarbonate and N-bromosuccinimide in water,¹⁴ unidentified water soluble products were obtained. When the dioxime was treated with N-bromosuccinimide in carbon tetrachloride solution at either -5 or 25 °C, DCF was obtained. Chlorination of the dioxime 4 at -60°C also produced DCF,3.

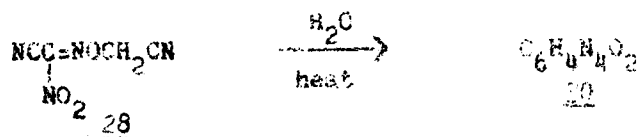
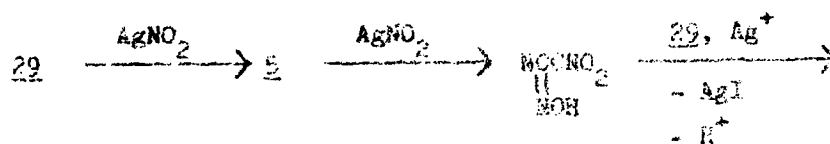
4. Dehydrodimerization of Nitroacetonitrile 5.

A compound 26, $\text{C}_4\text{H}_2\text{N}_4\text{O}_3$, (not identical with 22) was tentatively given the structure of dicyanomethazonic acid 27.¹⁵ A reassignment as the cyanomethyl ether 28 of nitrocyanocarbonyl is supported by

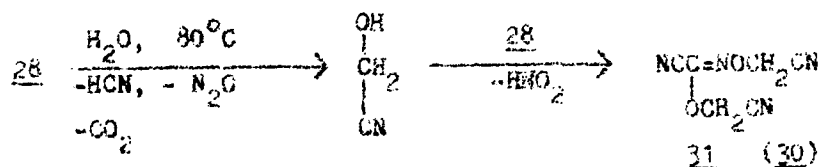
elemental analysis, mass spectrometry, and nmr and ir spectroscopy. It was obtained on the treatment of iodoacetoneitrile 29 with silver nitrite.¹⁵ The intermediacy of nitroacetoneitrile 5 is assumed.



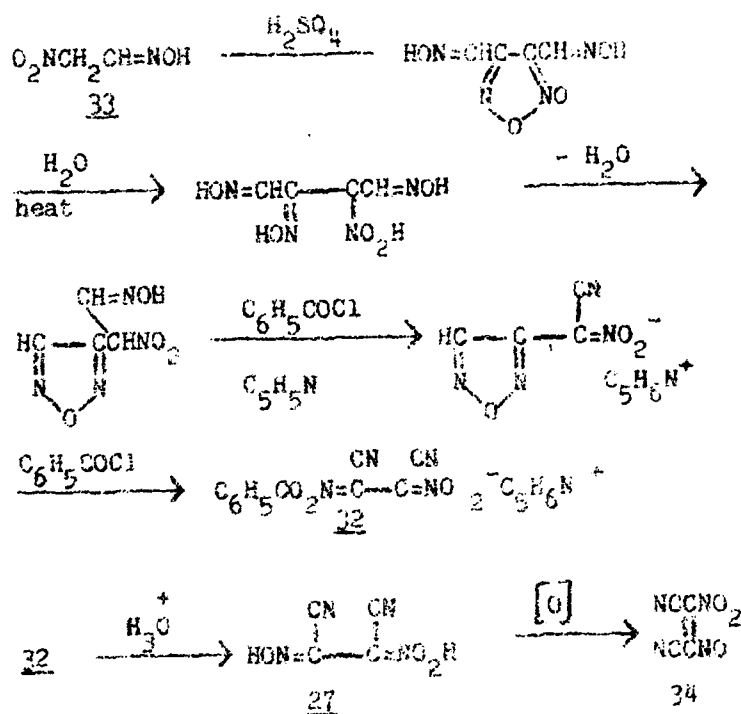
On heating in water compound 26 (28) was transformed into compound 30, $\text{C}_6\text{H}_4\text{N}_4\text{O}_2$, previously unidentified.¹⁵ The assignment as the cyano-methyl ether 31 of cyanomethylcyanohydroximate is supported by elemental analyses, mass spectrometry, and nmr and ir spectroscopy. A rationale for these reactions is shown.



THIS PAGE IS BEST QUALITY PRACTICABLE
FROM CONFIDENTIAL SOURCE

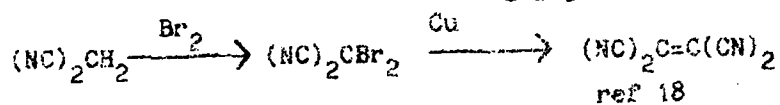
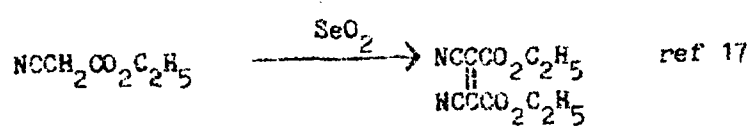
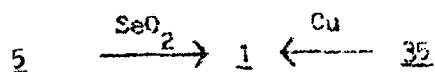
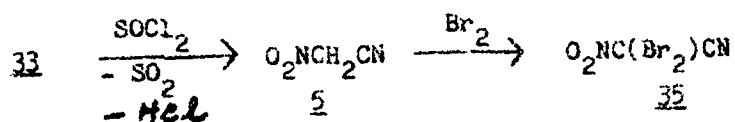


A pyridinium salt 32 of the O-benzoyloxime derivative of compound 27 was recently reported by Grundmann.¹⁶ His preparation of 27 from methazonic acid 33, shown in the scheme, has been repeated since an authentic compound 27 should be easily dehydrogenated into nitronitrosomaleonitrile 34 (or the isomeric fumaronitrile).



Methazonic acid 32 has also been transformed by thionyl chloride into nitroacetonitrile 5.¹⁶ Dehydrodimerization of the latter by selenium dioxide and by debromination of the dibromo derivative 35 are under investigation. Known model reactions are also shown in the scheme.

THIS PAGE IS BEST QUALITY PRACTICABLE



THIS PAGE IS BEST QUALITY PRACTICABLE
FROM GPO COPY 100-100000

References

1. L. E. Hinkel, G. O. Richards and O. Thomas, J. Chem. Soc., 1937, 1432.
2. Y. Ohtsuka, J. Org. Chem., 1976, 41, 629.
3. P. S. Robertson and J. Vaughan, J. Amer. Chem. Soc., 1958, 80, 2691.
4. R. G. Begland, D. R. Hartler, F. N. Jones, D. J. Sam, W. A. Sheppard, O. W. Webster and F. J. Weigert, J. Org. Chem., 1974, 39, 2341.
5. For many references, cf. H. O. House, Modern Synthetic Reactions, 2nd ed., W. A. Benjamin Inc., New York, 1972, pp 310-312.
6. Y. Ohtsuka, J. Org. Chem., 1979, 44 827.
7. R. W. White and W. D. Emmons, Tetrahedron, 1962, 17, 31.
8. R. P. Welcher, M. E. Castellion and V. P. Wystrach, J. Amer. Chem. Soc., 1959, 81, 2541.
9. R. G. Begland, D. R. Hartler, D. S. Donald, A. Cairncross and W. A. Sheppard, J. Org. Chem., 1974, 39, 1235.
10. D. Shew, Ph.D. Thesis, Indiana University, 1959.
11. C. O. Parker, W. D. Emmons, H. Z. Rojewicz and K. S. McCallum, Tetrahedron, 1962, 17, 87.
12. a. W. Wislicenus and R. Crutzner, Chem. Ber., 1909, 42, 1930.
b. Ch. Grundman, V. Mini, J. M. Dean and D. Frommelt Ann., 1965, 687, 191.
13. a. K. H. Pausacker, J. Chem. Soc., 1953, 1989.
b. G. B. Barlin, K. H. Pausacker and N. V. Riggs, J. Chem. Soc., 1954, 3122.

THIS PAGE IS BEST QUALITY PRACTICABLE
FROM COPY FURNISHED TO DDC

14. a. Don C. Iffland and G. X. Criner, J. Am. Chem. Soc., 1953, 75, 4047.
b. Don C. Iffland and T. Fu. Yen, J. Am. Chem. Soc., 1954, 76, 4083.
15. R. Scholl, Chem. Ber., 1901, 34, 862; 1896, 29, 2415.
16. C. Grundmann, G. W. Nickel and R. K. Bansal, J. L. Ann., 1975, 1029.
17. D. G. I. Felton, J. Chem. Soc. I 1955, 515.
18. T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKirsick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, J. Amer. Chem. Soc., 1958, 80, 2775.